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CHLORINATION OF NICKEL MINERALS

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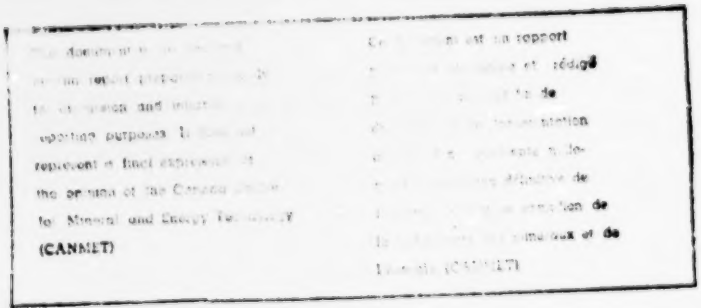

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CHLORINATION OF NICKEL MINERALS

by

S.A. Mikhail* and C.R.K. MacLean**

ABSTRACT

The interaction of nickeline (NiAs), millerite (NiS) and gersdorffite (NiAsS) with chlorine gas was studied using differential thermal analysis. Nickeline and millerite showed no noticeable activities in chlorine below 400°C. Above this temperature, both minerals started to chlorinate and a product layer of nickel chloride was formed on the surface of the particles. The chlorination was not complete before reaching 800°C. In the case of gersdorffite, chlorination started around 150°C and was almost complete below 400°C. Under certain circumstances, pyrite impurity or addition was found to enhance the chlorination of nickeline and millerite at lower temperatures.

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INTRODUCTION

High-temperature chlorination of uranium ores is currently under investigation at CANMET as a new process for uranium extraction (1,2). In this process, the uranium ore, containing sulphur compounds, is reacted with chlorine gas, with sulphur from the minerals acting as a reducing agent, to form UCl_4.

Mineralogical studies by D. Harris of uranium ores from Saskatchewan, namely, samples from Canada Wide Minerals, Midwest Lake, and Key Lake, have indicated the presence of substantial amounts of nickel minerals such as nickeline (NiAs), millerite (NiS) and gersdorffite (NiAsS). A feasibility study for the recovery of nickel from these minerals during the chlorination of the uranium ores is under consideration.

In the present work, the behaviour of the individual nickel minerals during interaction with chlorine was studied by differential thermal analysis (DTA). X-ray diffraction, electron microprobe analysis and spectrochemical analysis were used in the identificaton of the starting materials and the reaction products. The influence of the presence of pyrite, a mineral already present in the ores, and sodium chloride was also studied.

MATERIALS AND EXPERIMENTAL PROCEDURE

Nickeline (niccolite, NiAs) mineral samples from Cobalt, Ontario and the North West Territories, millerite (NiS) from Kambalda, Australia, and gersdorffite (NiAsS) from the North West Territories and from Montana, USA, were used in the present work. Synthetic NiAs and NiS were also used. Pyrite mineral from Colorado, USA, and reagent grade NaCl from Baker Chemical Co. were employed as additions in some experiments.

X-ray diffraction, spectrochemical analysis and microprobe analysis were used in the identification of the starting materials. The nickeline of Cobalt, Ontario was found to contain minor amounts of gersdorffite and traces of iron (0.06%) and cobalt (0.11%) while that from the North West Territories was found to be very pure mineral. The

millerite of Kambalda, Australia, contained pyrite, chalcopyrite (iron about 1.3%), and gangue. The N.W.T. gersdorffite contained minor amounts of pyrite, chalcopyrite, quartz, mica, chlorite, iron (about 4%) and cobalt (0.4%), and that from Montana, USA was found to be a pure mineral with less than 1% pyrite.

Differential thermal analysis (DTA) was used to study the chlorination reactions and X-ray diffraction, microscopic examination and solubility tests were used to identify the reaction products. The DTA assembly was designed to handle corrosive atmospheres. The experimental arrangement and procedure were previously reported in detail (3).

In preliminary tests, various sample weights and particle sizes were examined. A sample weight of 30-35 mg and a particle size of less than 38 μm (-400 mesh) were found most convenient and hence were used in all experiments. High purity (99.5%) chlorine from Matheson and high purity (99.997) argon from Linde were used after being dried by passing through calcium chloride. A chlorine flow rate of 60-80 ml/min and a heating rate of about 8°C/min were maintained in all experiments. DTA diagrams of nickeline and gersdorffite in an argon atmosphere did not indicate any noticeable thermal activities up to 800°C. The diagram for millerite showed an endothermic peak around 350°C indicating the transition from the low- to the high-temperature modification.

RESULTS AND DISCUSSION

NICKELINE (NiAs):

The DTA diagrams for the chlorination of nickeline are shown in Figure 1. The interaction of NiAs with chlorine gas started around 500°C in the case of pure nickeline or synthetic NiAs (Fig. 1b and 1c) and around 380°C in the case of impure nickeline (Fig. 1a). Below these temperatures no marked activities were noticed. In all cases, however, complete chlorination was not achieved below 800°C, at which temperature the $NiCl_2$ product started to volatilize.

The chlorination reaction may take place according to the following scheme:

$$NiAs + 2\tfrac{1}{2}Cl_2 \rightarrow NiCl_2 + AsCl_3$$

At the reaction temperature, a product layer of $NiCl_2$ forms on the surface of the arsenide particle while arsenic chloride, having a relatively low boiling point of 63°C, volatilizes instantly to be carried away by the gas stream. Further chlorination may take place by diffusion through the $NiCl_2$ product layer or when the product volatizes at higher temperatures.

In preliminary experiments, nickeline samples of different particle sizes were subjected to chlorination. The results showed that as the particle size increased (i.e. less available surface area) less exothermic activity (i.e. slower chlorination) showed on the diagrams at the lower temperatures. This may confirm that the reaction started at the gas-solid interface and as the product layer increased in thickness, the rate of reaction became controlled by diffusion through the product layer. Several experiments were interrupted at various stages of chlorination (at different temperatures) and the products were examined under the microscope, by X-ray diffraction and by testing their solubilities in water. The results always indicated the presence of nickel chloride and unchlorinated material in a ratio depending on the temperature at which the chlorination was interrupted.

An exothermic peak, which appeared consistently at 760-770°C (Fig. 1b and 1c), indicated further chlorination of nickeline in that temperature region. To clarify this behaviour, various mixtures of NiAs-$NiCl_2$ were heated in an argon atmosphere until molten in the DTA assembly. On cooling, an exothermic peak, which appeared on the DTA diagrams around 770°C and was common in all mixtures, may indicate a eutectic crystallization at that temperature. The chlorination peak at 760-770°C may therefore be explained on the basis of the eutectic melting which occurred at the NiAs-$NiCl_2$ interface causing a disruption of the product layer and allowing an access of Cl_2 to the unchlorinated core and hence the resumption of chlorination. Above 800°C, an endothermic trend on the diagrams indicated the volatilization of the $NiCl_2$ product which appeared as a cyrstalline precipitate on the inner surface of the reaction tube.

In the case of nickeline mineral from Cobalt, Ontario (low purity), some precipitate appeared on the reaction tube during the course of chlorination around 400°C. This may be due to chlorination

and volatilization of contained impurities. This did not happen in the case of the mineral from the North West Territories or the synthetic nickeline.

A series of experiments, in which nickeline was thoroughly mixed with various amounts of sodium chloride, of comparable particle size, and subjected to chlorination, was conducted. Almost complete chlorination was found to take place below 600°C. This may be attributed to the disruption of the $NiCl_2$ product layer by fusion in the presence of NaCl, and the exposure of the arsenide ore to further chlorination. The eutectic melting of a $NiCl_2$-NaCl mixture was reported to take place at 563°C (4). Figure 1d shows the DTA diagram of a mixture of nickeline and sodium chloride in chlorine.

The mineral pyrite was one of the major constituents in at least one of the uranium ores under investigation, and therefore a study of its influence on the chlorination of nickeline was found desirable. In a previous study (5), pyrite was found to interact with chlorine to form ferric chloride and sulphur chloride, both of which are also chlorinating agents. The chlorination of pyrite (-400 mesh particle size) started at room temperature and was complete around 250°C. The reaction products volatilized completely around 320°C (the boiling point of S_2Cl_2 is 138°C and of $FeCl_3$ is 315°C).

In another series of experiments, different nickeline/pyrite mixtures were subjected to chlorination in the DTA assembly. The results indicated that, for mixtures containing up to 20 wt % pyrite, selective chlorination of pyrite and complete volatilization of ferric chloride and sulphur chloride took place below 320°C without affecting the chlorination pattern of nickeline. However, when the amount of pyrite in the mixture was increased to 50 wt % and chlorine was introduced at temperatures above 200°C (unlike previous experiments where chlorine was introduced at room temperature), nearly complete chlorination of the sample took place below 500°C. The same result was obtained when pyrite was placed as a layer underneath, instead of mixed with, the nickeline sample. In the latter geometry, samples with 20 wt % pyrite were also mostly chlorinated below 500°C. The DTA diagram for the chlorination of a nickeline/pyrite mixture, Figure 1e, shows that a substantial chlorination took place between 240 and 400°C.

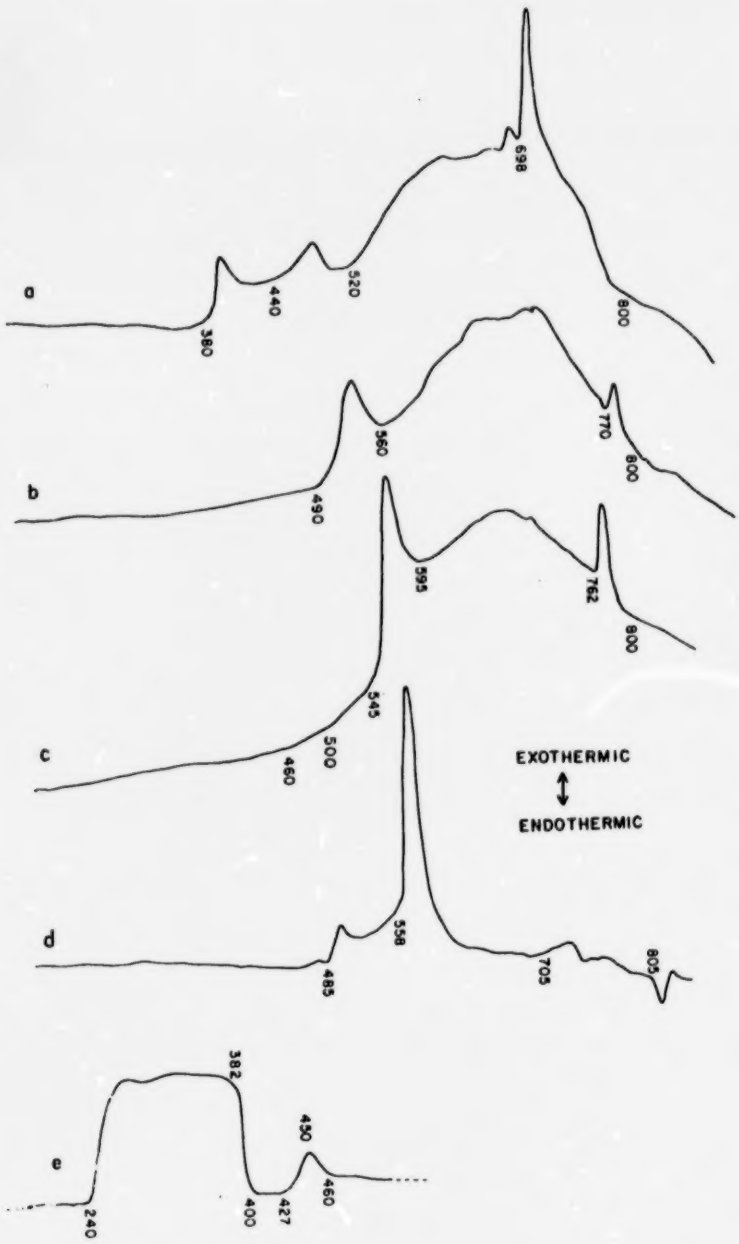

Fig. 1 DTA diagrams for the chlorination of nickeline
a. Nickeline from Cobalt, Ontario.
b. Nickeline from N.W.T.
c. Synthetic NiAs.
d. 90 wt % NiAs + 10% NaCl.
e. 50 wt % NiAs + 50% pyrite (Cl_2 introduced at 240°C)

MILLERITE (NiS):

The chlorination of the mineral millerite follows a similar pattern to that of the nickeline. The DTA diagrams for the chlorination of millerite alone and with additions are shown in Figure 2. In the case of synthetic NiS, Figure 2b, an endothermic peak representing the transformation to the high temperature modifiction appeared around 350°C. The first interaction between the NiS and chlorine took place at 440°C as indicated by an exothermic peak on the diagram. The chlorination continued as the temperature increased and was complete around 820°C. Some experiments were interrupted at different temperatures between 440 and 820°C and the samples were examined under the microscope, by X-ray diffraction and by solubility tests. Besides $NiCl_2$, unchlorinated material, in amounts depending on the temperature at which chlorination was interrupted, was detected.

In the presence of excess chlorine, the chlorination of millerite may proceed according to the following equation:

$$2NiS + 3Cl_2 \rightarrow 2NiCl_2 + S_2Cl_2$$

probably with further chlorination of S_2Cl_2 to SCl_2. The initial stages of reaction take place at the gas-solid interface and a product layer of $NiCl_2$ builds up at the surface of the sulphide particle while S_2Cl_2 volatilizes instantly as it forms (bp 138°C). Chlorination may then continue by diffusion through the product layer. An endothermic peak followed immediately by an exothermic activity appeared on the diagram around 800°C. This may be due to fusion, with disruption of the product layer exposing the unreacted core to further chlorination. For verification, various mixtures of NiS and $NiCl_2$ were prepared and examined by DTA in argon atmosphere. A prominent peak appeared consistantly around 800°C indicating the possibility of melting at this temperature.

The effect of particle size on the chlorination of millerite was also examined using DTA. The results indicated that the interaction of all particle sizes took place in the same temperature range (440-800°C). However, slower chlorination occurred with larger particle sizes (smaller surface area), and faster chlorination occurred with smaller particle sizes, at the lower end of the temperature range. In all cases, however, chlorination was never complete below 800°C.

The DTA diagram for the chlorination of the impure millerite from Kambalda, Australia, is shown in Figure 2a. It is noticeable that most of the exothermic activities, and hence substantial chlorination, took place below 400°C. This was also confirmed by examining the product after interrupting the chlorination at 550°C. This behaviour may be attributed to the chlorination of the pyrite inclusions to form $FeCl_3$, some of which, together with the $NiCl_2$ product, may form a liquid phase that disrupts the protective product layer allowing further contact of Cl_2 with the unreacted core. During the chlorination experiments, $FeCl_3$ and S_2Cl_2 precipitated on the colder parts of the reaction tube.

The effect of pyrite additions on the chlorination of millerite was studied separately by subjecting various mixtures of synthetic (pure) millerite and pyrite to chlorination in the DTA assembly. Nearly complete chlorination was observed below 500°C in a millerite/pyrite mixture of 1:1, Figure 2d, when chlorine was introduced around 300°C. Similar results were obtained when pyrite (20 wt %) was added as a layer underneath, instead of mixed with, the millerite sample. The different chlorination trends of the mineral which contained pyrite as impurity, Figure 2a, and the synthetic NiS with the pyrite addition, Figure 2d, may be attributed at least in part to the more intimate contact between the pyrite and the nickel sulphide in the former case. The latter series of experiments confirmed the positive influence of pyrite on the chlorination of millerite.

The influence of sodium chloride on the chlorination of millerite was also studied. Various mixtures of the two components were prepared and subjected to chlorination. Figure 2c shows a representative DTA diagram for a mixture of 90 wt % synthetic millerite and 10% NaCl. The results of this series of experiments indicated that the presence of sodium chloride led to a substantial chlorination below 600°C. Selected samples were examined after interrupting the chlorination around 600°C and were found to be mostly chlorinated. In the presence of NaCl, the product layer of $NiCl_2$, formed at the early stages of chlorination, seems to collapse on fusion at the $NiCl_2$-NaCl eutectic temperature, 563°C, allowing access of Cl_2 to the unchlorinated sulphide core underneath. It is also noticeable, in this series, that some chlorination has consistently taken place at the temperature of transformation (around 350°C) in presence of NaCl, Figure 2c.

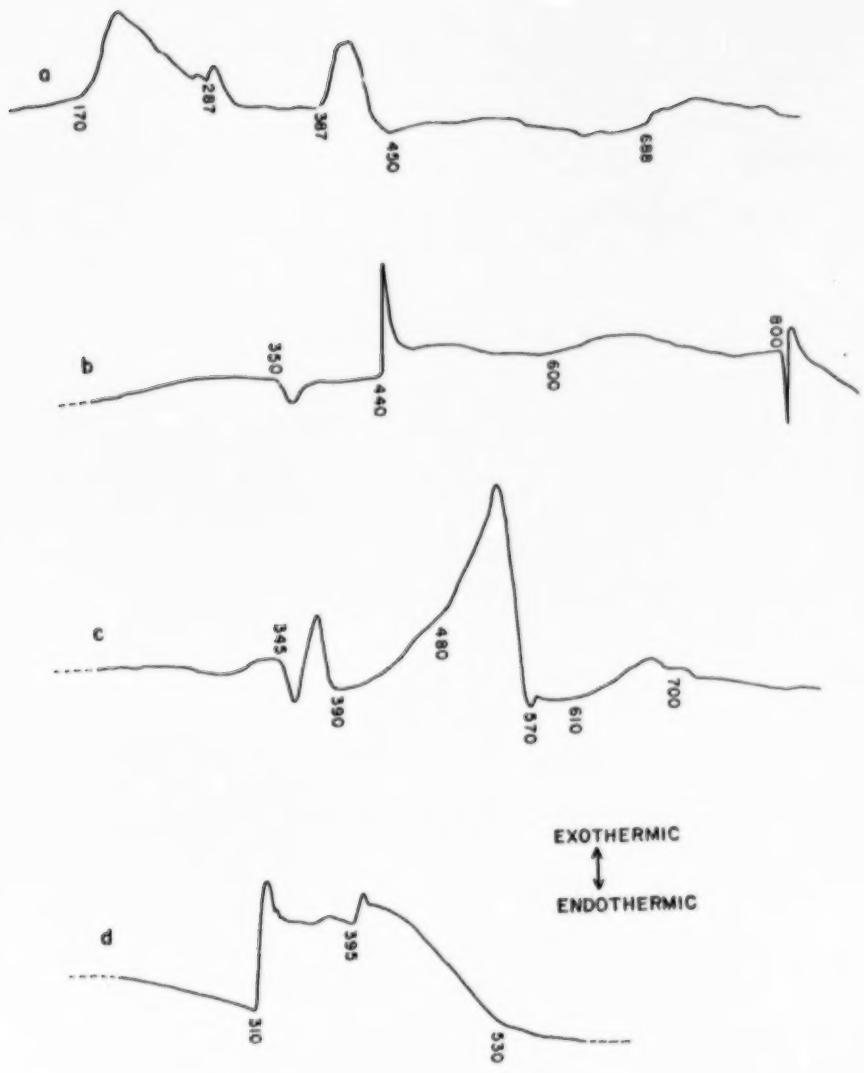

Fig. 2. DTA diagrams for the chlorination of millerite
a. Millerite from Kambalda, Australia
b. Synthetic NiS
c. 90 wt % NiS + 10% NaCl
d. 50 wt % NiS + 50% pyrite (Cl_2 introduced at 300°C)

GERSDORFFITE (NiAsS)

The chlorination of two gersdorffite minerals with different purities were examined and representative DTA diagrams are shown in Figures 3a and 3b. The high-purity mineral from Montana was found to chlorinate in the temperature range 185-350°C as indicated by the exothermic activities on the diagram, Figure 3a. Some experiments were interrupted at 400°C and the product was identified by X-ray diffraction to be $NiCl_2$ (traces of unchlorinated material were observed under the microscope). The total reaction of gersdorffite with chlorine may take place according to the following scheme:

$$2NiAsS + 6Cl_2 \rightarrow 2NiCl_2 + 2AsCl_3 + S_2Cl_2$$

Further chlorination of S_2Cl_2 to SCl_2 may also occur. The boiling points of $AsCl_3$ and S_2Cl_2 are 63 and 138°C respectively. Sulphur chloride was observed on the colder part of the reaction tube while arsenic chloride seemed to be carried away with the gas stream.

Figure 3b shows a representative DTA diagram for the chlorination of the gersdorffite mineral from the North West Territories (lower purity). It can be seen that substantial chlorination took place in the temperature range 150-300°C. When the chlorination was interrupted around 400°C and the product was examined under the microscope and by X-ray diffraction, slightly more unchlorinated material was found in the $NiCl_2$ matrix. The slight difference between the chlorination trends of the two minerals, Figures 3a and 3b, could be attributed to the presence of different types and amounts of impurities in the samples.

A few experiments were conducted by adding different amounts of pyrite to the gersdorffite mineral before chlorination. No marked difference, however, was observed in the chlorination trend. This result was predictable since the chlorination of gersdorffite takes place within (not above) the temperature range at which pyrite itself chlorinates and its reaction products volatilize.

In another series of experiments, various amounts of NaCl were mixed with gersdorffite for chlorination in the DTA assembly. The DTA diagram of a mixture of 95 wt % gersdorffite and 5% NaCl is shown in Figure 3c. In general, the effect of NaCl on the chlorination was found to be limited to dilution. The temperature of the start of chlorination

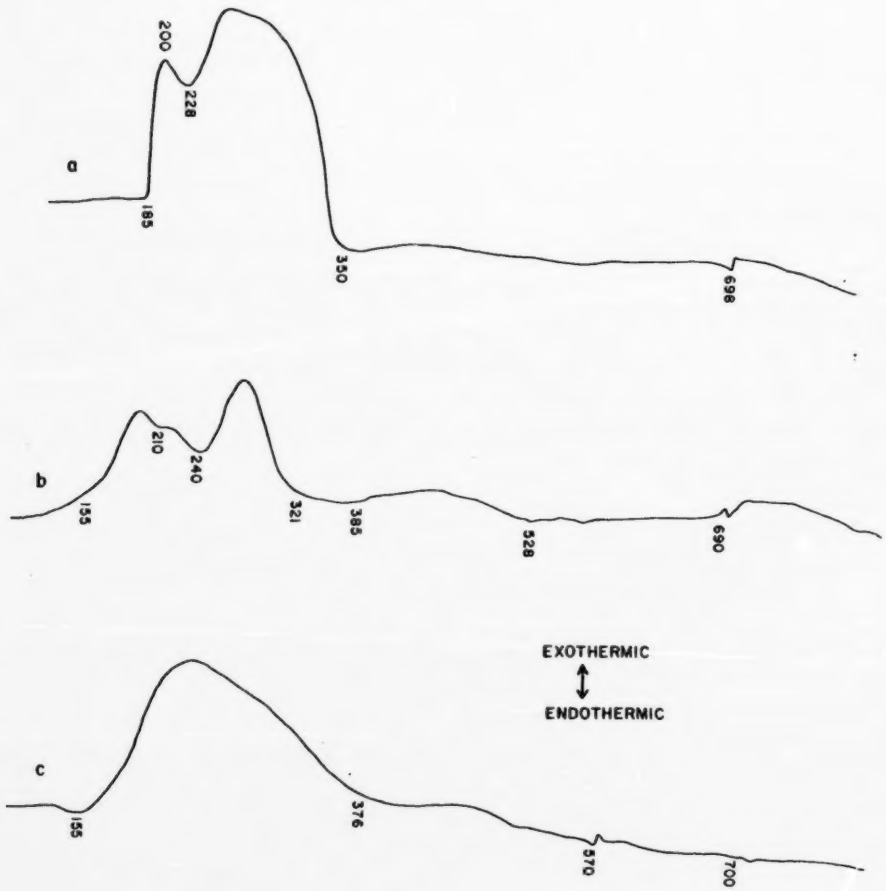

Fig. 3. DTA diagrams for the chlorination of gersdorffite.
a. Gersdorffite from Montana, U.S.A.
b. Gersdorffite from N.W.T.
c. 95 wt % gersdorffite + 5% NaCl.

was not altered by the addition and the end of the exothermic activities seemed to happen at slightly higher temperature. Nearly complete chlorination took place below 400°C.

CONCLUSIONS

The interaction of the minerals nickeline, millerite and gersdorffite with chlorine gas was studied using differential thermal analysis. Chlorination activities of nickeline and millerite were fairly similar and were found to take place in the temperature range 400-800°C forming nickel chloride. Under certain conditions, the addition of pyrite or NaCl enhanced the chlorination of both minerals at lower temperatures. The mineral gersdorffite was found to chlorinate completely below 400°C. The addition of pyrite or NaCl did not affect its interaction with chlorine to any significant extent.

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